Solvent Effects on the Absolute Intensities of Infrared Absorption Bands and the Dipole-Dipole Interaction

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The absolute intensities of the infrared absorption bands, ν_3 of methyl iodide, ν_2 of methyl cyanide, and ν_8 of methyl cyanide, were measured in various solvents at various concentrations. Even after the effect of the internal field is eliminated, very large solvent effects remain in the absorption intensities due to the intermolecular interactions. An equation based on the model of the dipole-dipole interaction is proposed to interpret the experimental results. Comparison with the experimental data confirms the validity of the model.

Much attention has been given to the change of infrared intensities in going from the gas to the liquid phase or from the gas phase to solutions. Many equations have been proposed to predict the ratio of the intensities of the gas and the liquid phases, among which that of Polo and Wilson1) is the most familiar. Mallard and Straley2) and Person3) proposed an equation for the intensity ratio of the gas phase and solutions, which is identical to that of Polo and Wilson to the limit of pure liquid. These two equations deal with the integrated intensities and neglect the anomalous dispersion of the refractive index in the region of the adsorption band. The validity of the assumption of a single refractive index was studied theoretically by Schatz.4) Although Schatz claims that the equation of Polo and Wilson is valid even for strong absorption bands if one chooses an appropriate value for the single refractive index, its usefulness is restricted to rather weak absorption bands.5) The same problem has been treated by many other authors.6–9) In the case of very strong absorption bands, one must take into account the frequency dependence of the refractive index rigorously, as shown theoretically and experimentally by Bakhshiev and coworkers10) and by Crawford and coworkers.11) These authors have presented an equation giving the relation between the apparent and the true absorption indices at each frequency. It is accepted that, when one compares the observed intensities at various phases, one must make a correction for the effect of the so-called internal field according to the scheme of Polo-Wilson or Mallard-Straley-Person for a weak absorption band and of Bakhshiev-Crawford for a strong absorption band. After being undergoing correction following the aforementioned schemes, the intensities of liquids or solutions agree well with the gas-phase intensities, if no specific solute-solute or solute-solvent interaction in liquids or solutions exists.6,10–12)

It should be noted that the above treatment deals only with the change of the internal field surrounding an absorbing molecule and does not consider the effects of intermolecular interactions. Some authors such as Buckingham,13) Mirone,14) and Bakhshiev and coworkers15) have discussed the effects of intermolecular interactions on infrared intensities. They used the reaction field of Onsager.16) Experimental works concerning these theories are very scarce.17–20)

In the present paper, the authors report the absolute intensities of a few absorption bands of methyl iodide and methyl cyanide in various solvents at various concentrations, and show that the effects of solvents are very large in some cases, even after the elimination of the effect of the internal field. The vibrational bands and solvents are as follows, ν_3 (the C–I stretching vibration) of methyl iodide, solvents: methyl cyanide and carbon disulfide, ν_2 (the C≡N stretching vibration) of methyl cyanide, solvents: carbon tetrachloride and 1,1,1-trichloroethane, and ν_8 (the CCN bending vibration) of methyl cyanide, solvents: carbon tetrachloride and nitromethane. In these systems no serious specific solute-solute or solute-solvent interaction is expected other than the dipole-dipole interaction. An equation is proposed to connect the absolute intensity of a pure liquid or a solution to that of the gas phase, based on the model of the dipole-dipole interaction.

Experimental

Commercial chemicals were used. Methyl iodide was distilled just before the observation to remove the pale yellowish color. Other samples were used without further purification although the infrared spectrum of methyl cyanide showed a samll amount (about 0.5 wt%) of water in it: the presence of water in methyl cyanide seems to cause no serious error.

Binary solutions were prepared just before the observation to attain appropriate concentrations by measuring the weight of each component. Mole percentage and molar concentrations were calculated by use of the density data.21) Additivity of the volumes of both components was assumed.

The infrared spectra of the ν_2 band of methyl cyanide were measured in carbon tetrachloride- and 1,1,1-trichloroethane-solutions at various concentrations with a Perkin-Elmer 112G single-beam infrared spectrometer. A Perkin-Elmer 12C single-beam infrared spectrometer mounted with a CsBr prism was used to measure the ν_8 band of methyl cyanide in carbon tetrachloride- and nitromethane- solutions. The same spectrometer mounted with a KBr prism was used to measure the ν_3 band of methyl iodide in methyl cyanide- and carbon disulfide-solutions. The frequencies were calibrated following the standard method with the use of atmospheric water-vapour or carbon dioxide lines for the 112G spectrometer, and atmospheric water-vapour and methanol vapor lines for the 12C spectrometer.22) The spectrometers were operated under a resolution of about 1 cm^{-1} except for the case of the ν_8 band of methyl cyanide, where the resolution was about 2 cm^{-1}. The effect of the finite slit width on the observed spectra was found to be very small. It was confirmed that the observed spectra were free of stray-light. All the measurements were carried out at room temperature

(25 °C). Each spectrum was measured at least twice.

A variable-length cell with KRS-5 window was used in the measurements. The thickness of the sample-cell was determined at each observation by the method of interference fringes.[23]

The observed spectra were reduced to the absorption-index curves, $k(\nu)$'s[24] where ν is the wavenumber in cm^{-1}, and the absolute intensities, Γ's, were calculated by means of the definition:[25]

$$\Gamma = \frac{4\pi}{c_{\mathrm{m}}}\int_{\mathrm{band}} k(\nu)\ \mathrm{d}(\nu)$$

where c_{m} is the molar concentration (mol/cm^3). The integration of $k(\nu)$ over the absorption band was estimated by fitting a Lorentzian curve to the observed $k(\nu)$ curve by the method of least-squares. Care should be taken so that all the observed absorption bands contain hot bands in their lower-frequency sides. The hot bands cause the asymmetry of the main bands and it was found to be difficult to remove them by the usual method of least-squares. Thus, only the high-frequency sides of the bands were used in numerical calculations. The standard deviations were estimated from the deviations of the calculated Lorentzian curves from the observed absorption curves and from the maximum errors in the thicknesses of the sample-cell.

Since all the observed absorption bands are weak, Mallard-Straley-Person's scheme[2,3] was applied to the correction for the effect of the internal field, according to the equation

$$\Gamma_{\mathrm{c}} = n_{\mathrm{s}}\left[\frac{(n/n_{\mathrm{s}})^2+2}{n^2+2}\right]^2\Gamma$$

where n_{s} and n are the refractive indices of the solution and the solute, respectively, and Γ_{c} is the corrected intensity which is to be compared with the intensity of the gas phase. The refractive index was measured by the use of an Abbe's refractometer for each solution at the room temperature. The absolute intensity, Γ_{c}, is related to the transition dipole moment, m_1, of the vibrational transition by the equation[26]

$$\Gamma_{\mathrm{c}} = \frac{8\pi^3}{3hc}N_{\mathrm{a}}(m_1)^2$$

where h is Planck's constant, c the velocity of light, and N_{a} Avogadro's number. The observed intensity, Γ_{c}, is shown at each concentration in Figs. 1—4. The values of Γ's, Γ_{c}'s, and $|m|$'s are given in Tables 1—3.

Results and Discussion

We see from the figures that the absolute intensities greatly change in solutions even after correction for the internal fields. This indicates that the transition moment, m_1, changes in solutions as a result of intermolecular interactions. Thus we can obtain information on intermolecular interactions in liquids or solutions from the experimental data. In the following, we deal with the theoretical consideration on the change of infrared intensity in solutions.

The electric dipole moment, m, of a molecule under the influence of electric field, $\mathfrak{F}$, is given by

$$m = \mu + \alpha\langle\mathfrak{F}\rangle_{\mathrm{av}} \tag{1}$$

where μ and α are the electric dipole moment and the electric dipole polarizability, respectively, of an isolated molecule, and molecule, and $\langle\ \rangle_{\mathrm{av}}$ means the average over all possible configurations of the surrounding molecules. All the quantities appearing in Eq. (1) can be expanded in powers of the normal coordinates of the vibrations. In the expansion of m, we take only the term that is linear on the normal coordinate, q, of the vibration:

$$m_1 = \mu_1 + \alpha_1\langle\mathfrak{F}_0\rangle_{\mathrm{av}} + \alpha_0\langle\mathfrak{F}_1\rangle_{\mathrm{av}} \tag{2}$$

where the suffixes "0" and "1" mean respectively the zeroth and the first terms of the expansion, namely:

$$A_0 = \langle 0|A|0\rangle \tag{3}$$

and

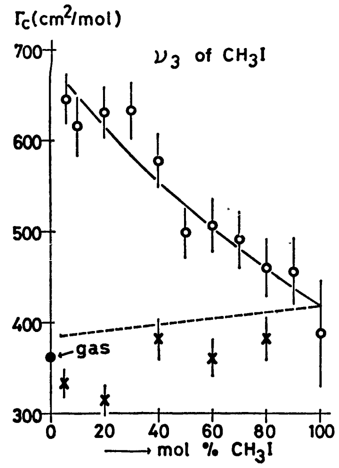

Fig. 1. Concentration-dependence of the absolute intensity of the ν_3 band of methyl iodide. The open circles and crosses indicate the observed intensities in methyl cyanide-solutions and in carbon disulfide-solutions, respectively. The vertical lines indicate standaed deviations. The solid line shows the concentration-dependence for methyl cyanide-solutions, calculated from the parameters of Table 4. The broken line shows the concentration-dependence for carbon disulfide-solutions, predicted from the same parameters of Table 4.

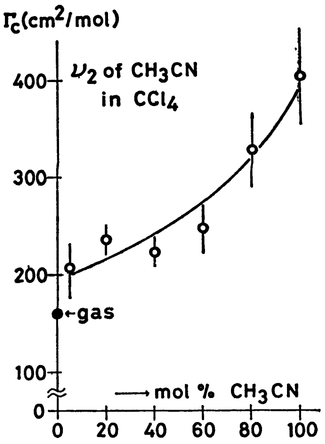

Fig. 2. Concentration-dependence of the absolute intensity of the ν_2 band of methyl cyanide in carbon tetrachloride-solutions. The open circles indicate observed intensities and the vertical lines standard deviations. The solid line shows the concentration-dependence calculated from the parameters of Table 4. The closed circle corresponds to the gas-phase intensity of Jesson and Thompson.[33]

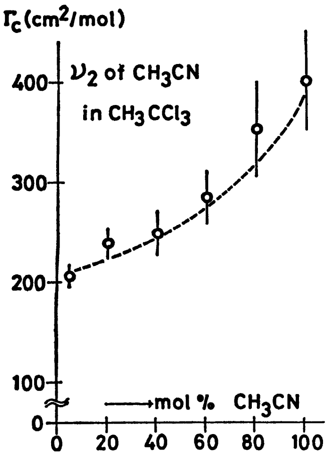

Fig. 3. Concentration-dependence of the absolute intensity of the ν_2 band of methyl cyanide in 1,1,1-trichloroethane-solutions. The open circles indicate observed intensities and the vertical lines standard deviations. The broken line shows the concentration dependence predicted from the parameters of Table 4.

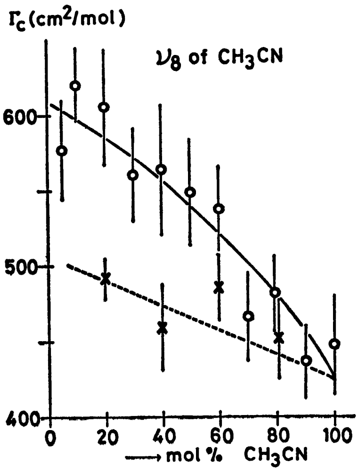

Fig. 4. Concentration-dependence of the absolute intensity of the ν_8 band of methyl cyanide. The open circles and crosses indicate the observed intensities in carbon tetrachloride-solutions and in nitromethane-solutions, respectively. The vertical lines indicate standard deviations. The solid line shows the concentration-dependence for carbon tetrachloride-solutions, calculated from the parameters of Table 4. The broken line shows the concentration-dependence for nitromethane-solutions, predicted from the same parameters of Table 4.

$$A_1 = \left(\frac{\partial A}{\partial q}\right)\langle 0|q|1\rangle \qquad (4)$$

The calculation of $\langle \mathfrak{F}_0 \rangle_{av}$ and $\langle \mathfrak{F}_1 \rangle_{av}$ has been made by Buckingham[13] and Bakhshiev and coworkers[15] using the reaction field of Onsager:[16] their results are expressed in terms of the dielectric constants of the surrounding macroscopic media. On the other hand, the present authors have recently calculated $\langle \mathfrak{F}_0 \rangle_{av}$ based on a model of dipole-dipole interaction to explain the equilibrium of *trans*- and *gauche*-1,2-dibromoethanes in the liquid and in solutions,[27] and have shown that the latter calculation explains well the part of the averaged electric field that changes in solutions, although the absolute value does not agree with that calculated from the reaction field. We calculated $\langle \mathfrak{F}_0 \rangle_{av}$ and $\langle \mathfrak{F}_1 \rangle_{av}$ following the same model of dipole-dipole interaction as before.

TABLE 1. CONCENTRATION-DEPENDENCE OF THE ABSOLUTE INTENSITY OF THE ν_3 BAND OF METHYL IODIDE
(Values in parentheses are standard deviations)
ν_3 of methyl iodide

mol%	Γ (cm^2/mol)	Γ_c (cm^2/mol)	$\lvert m_1$(obsd)$\rvert$ (Debye)	$\langle \mathfrak{F}_p \rangle_{av} \times 10^{-6}$ (Debye/cm^3)
	—methyl cyanide-solution—			
100	531 (79)	388 (58)	0.0393	0.0151
90	621 (49)	456 (36)	0.0427	0.0232
80	622 (42)	460 (31)	0.0428	0.0333
70	660 (41)	491 (31)	0·0443	0.0410
60	678 (39)	507 (29)	0.0450	0.0501
50	662 (36)	498 (27)	0.0446	0.0600
40	762 (39)	578 (29)	0.0480	0.0699
30	831 (40)	633 (31)	0.0502	0.0827
20	823 (36)	631 (28)	0.0502	0.0912
10	799 (42)	616 (32)	0.0496	0.1044
6	836 (35)	646 (27)	0.0508	0.1087
	—carbon disulfide-solutions—			
80	525 (32)	382 (23)	0.0390	0.0121
60	498 (27)	361 (20)	0.0379	0.0091
40	527 (30)	381 (22)	0.0390	0.0061
20	436 (23)	314 (16)	0.0354	0.0031
5	463 (21)	333 (15)	0.0364	0.0008

TABLE 2. CONCENTRATION-DEPENDENCE OF THE ABSOLUTE INTENSISITY OF THE ν_2 BAND OF METHYL CYANIDE
(Values in parentheses are standard deviations)
ν_2 of methyl cyanide

mol%	Γ (cm^2/mol)	Γ_c (cm^2/mol)	$\lvert m_1$(obsd)$\rvert$ (Debye)	$\langle \mathfrak{F}_p \rangle_{av} \times 10^{-6}$ (Debye/cm^3)
	—carbon tetrachloride-solutions—			
100	480 (59)	401 (49)	0.0400	0.3980
80	393 (44)	326 (37)	0.0360	0.2717
60	298 (29)	246 (24)	0.0313	0.1776
40	272 (19)	223 (15)	0.0299	0.1051
20	288 (18)	235 (15)	0.0306	0.0463
5	254 (29)	207 (24)	0.0288	0.0111
	1,1,1-trichloroethane-solutions—			
80	426 (57)	353 (47)	0.0375	0.2724
60	345 (32)	285 (26)	0.0337	0.1837
40	303 (27)	249 (22)	0.0315	0.1188
20	292 (19)	239 (15)	0.0309	0.0661
5	251 (14)	206 (11)	0.0287	0.0334

The basic idea of the model is that the solute and the solvent molecules are dispersed uniformly and homogeneously in a vacuum instead of in a continuous dielectric medium. Each molecule has its physical quantities (say, dipole moment, polarizability, *etc.*) identical with those in the gas phase, but since the density is so high (or the average intermolecular separation between the nearest neighbour is so short) in the

TABLE 3. CONCENTRATION-DEPENDENCE OF THE ABSOLUTE INTENSITY OF THE ν_8 BAND OF METHYL CYANIDE
(Values in parentheses are standard deviations)
ν_8 of methyl cyanide

mol%	Γ (cm²/mol)	Γ_c (cm²/mol)	$\lvert m_1(\text{obsd})\rvert$ (Dybye)	$\langle\mathfrak{F}_p\rangle_{av}\times10^{-6}$ (Debye/cm³)
	—carbon tetrachloride-solutions—			
100	536(40)	447(33)	0.0422	0.3980
90	524(28)	436(24)	0.0417	0.3355
80	581(31)	481(25)	0.0438	0.2726
70	565(36)	466(29)	0.0431	0.2263
60	652(34)	537(28)	0.0463	0.1782
50	667(42)	548(35)	0.0468	0.1450
40	686(52)	563(43)	0.0474	0.1020
30	684(38)	560(31)	0.0473	0.0735
20	740(46)	605(38)	0.0491	0.0488
10	759(29)	620(24)	0.0497	0.0222
5	706(41)	577(33)	0.0480	0.0120
	—nitromethane-solutions—			
80	543(33)	452(28)	0.0425	0.3621
60	584(27)	485(22)	0.0440	0.3246
40	553(34)	459(28)	0.0428	0.2838
20	593(16)	491(13)	0.0443	0.2501

liquid phase or in solutions, the magnitudes of these quantities are modified as a consequence of intermolecular interactions, a typical example being Eq. (2). Following the same procedure as before, we obtain:[27]

$$\langle\mathfrak{F}_0\rangle_{av}=\frac{4\pi^2}{27}N_a{}^2\mu_0\left[\left(\frac{\mu_0{}^2}{kT}+\alpha_0\right)\frac{\rho}{W_m}c_m+\left(\frac{\mu_{0s}{}^2}{kT}+\alpha_{0s}\right)\right]+\frac{2\pi^4}{25\times243}N_a{}^4\mu_0\times\left[\frac{\mu_0{}^6}{(kT)^3}\left(\frac{\rho}{W_m}\right)^3c_m+\frac{\mu_0{}^2\mu_{0s}{}^4}{(kT)^3}\frac{8^3}{A^3}c_{ms}\right] \tag{5}$$

$$\langle\mathfrak{F}_1\rangle_{av}=\frac{4\pi^2}{27}N_a{}^2\mu_1\left[a_0\frac{\rho}{W_m}c_m+a_{0s}\frac{8}{A}c_{ms}\right] \tag{6}$$

where

$$A=\left\{\left(\frac{W_m}{\rho}\right)^{1/3}+\left(\frac{W_{ms}}{\rho_s}\right)^{1/3}\right\}^3 \tag{7}$$

and m_1, μ_1, α_0, and α_1 are those already described in Eq. (2), μ_0 is the permanent dipole moment of the solute molecule, W_m, ρ, and c_m are respectively the molecular weight, density, and molar concentration (mol/cm³) of the solute (the same symbols suffixed by "s" refer to those of the solvent), and N_a is the Avogadro number.

Calculation showed that $\langle\mathfrak{F}_1\rangle_{av}$ is very small as compared with $\langle\mathfrak{F}_0\rangle_{av}$ and that the terms containing α_0 and α_{0s} in the parentheses of the first term of Eq. (5) have much smaller contributions than the rest. We have therefore neglected these terms and analysed the experimental data by the following equation:[29]

$$m_1=\mu_1+\alpha_1\langle\mathfrak{F}_p\rangle_{av} \tag{8}$$

where

$$\langle\mathfrak{F}_p\rangle_{av}=\frac{4\pi^2}{27}N_a{}^2\mu_0\left[\frac{\mu_0{}^2}{kT}\frac{\rho}{W_m}c_m+\frac{\mu_{0s}{}^2}{kT}\frac{8}{A}c_{ms}\right]+\frac{2\pi^4}{25\times243}N_a{}^4\frac{\mu_0{}^3}{(kT)^3}\left[\mu_0{}^4\left(\frac{\rho}{W_m}\right)^3c_m+\mu_{0s}{}^4\frac{8^3}{A^3}c_{ms}\right] \tag{9}$$

Equation (8) relates the intensity data and the parameters, μ_1 and α_1. We can thus determine the magnitudes of μ_1 and α_1, using the intensity data at different concentrations and the calculated $\langle\mathfrak{F}_p\rangle_{av}$. In the calculation of $\langle\mathfrak{F}_p\rangle_{av}$, permanent dipole moments were taken to be 3.92 D for methyl cyanide,[30] 1.65 D for methyl iodide,[30] 1.79 D for 1,1,1-trichloroethane,[31] and 3.10 D for nitromethane.[30] For the ν_3 transition of methyl iodide, we obtained $|\mu_1|$ of 0.0391 D and $|\alpha_1|$ of 0.1134 Å³ from the experimental data of methyl cyanide-solutions by the method of least squares. Similarly, we obtained $|\mu_1|$ and $|\alpha_1|$ for the ν_2 and the ν_8 transitions of methyl cyanide, both from the data of carbon tetrachloride-solutions. The obtained values of $|\mu_1|$ and $|\alpha_1|$ are given in Table 4. The calculated concentration-dependence of the absolute intensities, corresponding to the determined $|\mu_1|$ and $|\alpha_1|$, is shown by solid lines in Figs. 1, 2, and 4.

In order to confirm the validity of the present theory and the obtained parameter-values, the concentration-dependencies of the absolute intensity for the other solvents were calculated using the values of $|\mu_1|$ and $|\alpha_1|$ of Table 4. The calculated curves are compared with the observed intensities in Figs. 1, 3, and 4 (broken lines).

We see that the agreement between the observed and the predicted concentration-dependence of the absolute intensities is fairly good for all the absorption bands. This indicates that the present model of dipole-dipole interaction can well represent the mechanism that causes a variation of the infrared absorption intensities in solutions. Incidentally, the gas-phase intensity data[32–34] are included in Figs. 1 and 2. It is seen that the calculated intensities approach the gas-phase intensities in the limit of the infinite dilution by nonpolar solvents, which indicates that the present estimation of $|\mu_1|$ is very reasonable. It should be noted that, although the signs of μ_1 and α_1 can not be determined from the intensity measurements, the signs of the products, $\mu_1\alpha_1$'s, can be determined from the solvent effect data. The conclusion is that $\mu_1\alpha_1>0$ for the ν_3 transition of methyl iodide, since as $\langle\mathfrak{F}_p\rangle_{av}$ becomes large so does $|m_1|$. Similarly we obtain the result $\mu_1\alpha_1>0$ for the ν_2 transition of methyl cyanide and $\mu_1\alpha_1>0$ for the ν_8 transition of methyl

TABLE 4. VALUES OF $|\mu_1|$ AND $|\alpha_1|$
(The values were determined by the method of least-squares from the data of methyl cyanide-solutions for ν_3 of methyl iodie, and from the data of carbon tetrachloride-solutions for ν_2 and ν_8 of methyl cyanide. Values in parentheses are standard deviations)

Transition	$\lvert\mu_1\rvert$ (D)	$\lvert\alpha_1\rvert$ (Å³)	$\mu_1\alpha_1$
ν_3 CH$_3$I	0.0391(0.0008)	0.1134(0.0114)	+
ν_2 CH$_3$CN	0.0280(0.0008)	0.0285(0.0039)	+
ν_8 CH$_3$CN	0.0493(0.0005)	0.0204(0.0022)	−

cyanide. Dickson *et al.*[32] concluded that $\mu_1<0$ for the ν_3 transition of methyl iodide. Thus we can say that $\alpha_1<0$ for this particular transition.

We must remember that the calculation of $\langle \mathfrak{F}_0 \rangle_{av}$, based on the same model as in the present paper, resulted in very different values from those calculated on the basis of the reaction field in the case of 1,2-dibromoethane in liquid and in solutions,[27] although the former can well explain that part of the field which changes in concentration- or temperature-variation. The same situation is expected for the present cases. If we have data for the dielectric constant as each concentration, and calculate $\langle \mathfrak{F}_p \rangle_{av}$ by use of the reaction field formalism, somewhat different values for $|\alpha_1'|$s from the present results may be obtained. Thus the present values of $|\alpha_1|$'s can not be too much relied upon. In fact, we obtain $|\alpha_1|$ of 0.11 Å^3 for the ν_2 transition of methyl cyanide, if we use the gas-phase absolute intensity of Raman scattering measured by Schrotter and Bernstein.[39] neglecting the anisotropy of α_1. It seems, however, that the present approach has something to do with the real mechanism of molecular interaction that causes the intensity change, from the fact that the two-parameter equation, Eq. (8), can reproduce the intensity change very well.

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24) M. Kakimoto and T. Fujiyama, This Bulletin, **45**, 3021 (1972), Eq. (1).

25) B. Crawford, Jr., *J. Chem. Phys.*, **29**, 1042 (1958), Eq. (2).

26) See, for example, J. Overend, "Quantitative Intensity Studies and Dipole Moment Derivatives," in "Infrared Spectroscopy and Molecular Structure," edited by M. Davies, Elsevier (1963).

27) M. Kakimoto and T. Fujiyama, This Bulletin, in press.

28) The second term of Eq. (5) arises from the third-order term in the expansion of the distribution function (see footnote 13) of the reference[27]). When the dipole moment is very large, as is the case for methyl cyanide, this term gives a significant contribution that can not be neglected.

29) The direction of $\langle \mathfrak{F}_0 \rangle_{av}$ or $\langle \mathfrak{F}_p \rangle_{av}$ in the present model is always the same as that of the permanent dipole moment. Therefore the rigorous expression for α_1 should be $(\alpha_{\rho\sigma})_{01}$ according to the notation of Placzek,[40] where ρ and σ indicate the directions of μ_1 and μ_0, respectively, in the molecular frame.

30) C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill (1955).

31) A. A. Maryott, M. E. Hobbs, and P. M. Gross, *J. Amer. Chem. Soc.*, **63**, 659 (1941).

32) A. D. Dickson, I. M. Mills, and B. Crawford, Jr., *J. Chem. Phys.*, **27**, 445 (1957).

33) J. P. Jesson and H. W. Thompson, *Spectrochim. Acta*, **13**, 217 (1958), referred to in B. H. Thomas and W. J. Orville-Thomas, *J. Mol. Structure*, **7**, 123 (1971), in the unit of 10^3 darks. We converted the latter into the unit of cm^2/mol by the relation:

$$\Gamma(\text{cm}^2/\text{mol}) = \text{A(darks)} \times 10^3/\nu_0$$

where ν_0 is the wavenumber (cm^{-1}) at the band center.

34) Kondo's preliminary result[35] is 103 darks or 272 cm^2/mol for the gas-phase intensity of the ν_8 band of methyl

cyanide, which conflicts with the present result. Among other authors, Gordon[36] reports 113 darks and Hendricks[37] reports 130 darks. It seems that some unexplained cause exists which makes the intensity of this particular absorption band in carbon tetrachloride-solution very different from that of the gas phase.

35) S. Kondo, private communication.

36) A. V. Gordon, Dissertation (Oxford University, 1954).

37) Hendricks, Ph. D. Thesis (Brown University, 1956), cited in the report of Names and Orville-Thomas.[38]

38) L. Names and W. J. Orville-Thomas, *Trans. Faraday Soc.*, **61**, 2612 (1965).

39) H. W. Schrötter and H. J. Bernstein, *J. Mol. Spectrosc.*, **12**, 1 (1964). It should be noted that the value of α_1 appearing in the equation of the Raman-intensities should not be precisely the same as that in the present discussion, bacause the dispersion formula of α_1[40] includes the frequency of the incident light. In the present discussion, α_1 corresponds to a static field, while the Raman scattering is usually excited by a visible light.

40) G. Placzek, "The Rayleigh and Raman Scattering," U. S. At. Energy Comm. UCRL-TRANS-526(L), 1962 [translated from "Marx Handbuch der Radiologie," Akademischer Verlagsgeselschaft, Leipzig(1934), 2nd ed., Vol. 6, Pt. II, pp. 205—374].